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A SIMPLE DWBA (FRANCK-CONDON) TREATMENT OF H-ATOM
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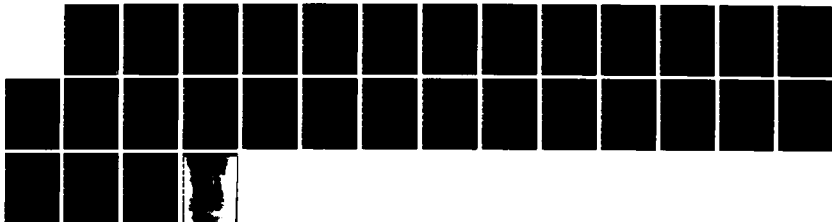
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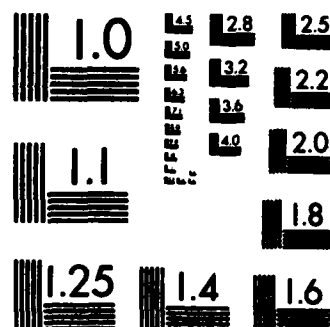
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20. ABSTRACT (continued)

reactants' and products' wavefunctions and the interaction potential. The reactants' and products' wavefunctions are calculated from their respective distortion potentials as one-term adiabatically separable approximations. Both the distortion potentials and the interaction potentials are extracted straightforwardly from the LEPS surface. The novel feature of the approach is that for the first time accurate results for the absolute values of the reaction probability are obtained from a simple overlap of single-channel approximate wavefunctions obtained directly from the respective parts of the potential energy surface for the reaction.



A1

**A simple DWBA ('Franck-Condon') treatment of H-atom transfers
between two heavy particles**

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A simple DWBA (Franck-Condon) method for calculating the probability of transferring a light particle between two heavy ones in a collinear collision at energies below and around the reaction threshold is presented. The region is the important one for the thermal reaction rates. The method is tested for two different model LEPS surfaces for H-atom transfer with moderately high barriers. The results are in good agreement with those of accurate multichannel calculations.

The transition probability is calculated as an overlap integral over the reactants' and products' wavefunctions and the interaction potential.

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The reactants' and products' wavefunctions are calculated from their respective distortion potentials as one-term adiabatically separable approximations. Both the distortion potentials and the interaction potentials are extracted straightforwardly from the LEPS surface. The novel feature of the approach is that for the first time accurate results for the absolute values of the reaction probability are obtained from a simple overlap of single-channel approximate wavefunctions obtained directly from the respective parts of the potential energy surface for the reaction.

1. INTRODUCTION

The rates of many chemical reactions at low and moderate temperatures are determined mainly by the reactive transition probabilities of energies below and around the classical reaction threshold. At such energies the scattering is predominantly inelastic and the reactive scattering probabilities are low. One can expect therefore that treating the reactive scattering as a perturbation to the much simpler inelastic scattering may yield a satisfactory simple method for evaluating the reactive transition probabilities in the threshold region, and hence for obtaining thermal reaction rates.

Treatments of this type, known as Distorted Wave Born Approximations (DWBA) for reactive collisions, have been extensively studied in recent years.¹⁻⁵ They consist in evaluating the reactive transition probability as an integral over two separate nonreactive wavefunctions, one corresponding to the reactants' and one to the products' configuration, and an exchange interaction operator. Further simplified versions of the treatment, known as Franck-Condon theories of chemical reactions, have also been frequently considered.⁶⁻¹⁷ One simplification consists in treating the interaction operator as a constant, which reduces the expression to an overlap integral between the two distorted wavefunctions. Utilizing analytical approximations to the distorted wavefunctions, usually in terms of Airy functions for the unbound motion and harmonic oscillator wavefunctions for the bound motion, also allows calculating an approximation to the transition probability in closed form, clearly at a further loss of accuracy.

At energies below the classical reaction threshold the main contribution to the DWBA integral comes from the exponentially decaying tail end

of the distorted wavefunctions.¹⁸ As a result, small displacements of the tail position can lead to errors of several orders of magnitude in evaluating the DWBA integral.^{5,11} Most of the work done using the DWBA approximation in reactive scattering has been actually concerned with evaluating the vibrational distributions of the products, and the absolute values of the transition probabilities have only rarely^{3,5,12} been evaluated.

More recently,¹⁹⁻²³ it has been shown that the DWBA formalism can yield accurate absolute values for the reactive transition probabilities in the threshold region if properly evaluated distorted wavefunctions and interaction potential are employed for the reactants and the products. We have developed¹⁹⁻²¹ a simple DWBA treatment of degenerate and nearly degenerate H-atom transfer reactions in which the distorted wavefunctions are constructed as a linear combination of two adiabatically separable wavefunction. The treatment has been shown to give excellent results for several model systems.¹⁹⁻²¹ Hubbard, Shi and Miller²³ have demonstrated that the DWBA approximation can give accurate results in the threshold region for the $H + H_2$ reaction, if converged distorted wavefunctions, extracted from an accurate coupled channel numerical solution of the complete Schrodinger equation for the problem, and the exact interaction operator, are utilized in the evaluation of the integral.

In this paper we develop a simpler version of our earlier DWBA treatment of the light atom transfer reactions.¹⁹⁻²¹ The present work is closer in spirit and simplicity to the Franck-Condon treatments⁶⁻¹⁷ but still retains the high accuracy of the transition probabilities for the light atom transfer reactions mentioned above.¹⁹⁻²² It is also not restricted to transfer between two degenerate or nearly degenerate vibrational states.

The distorted wavefunctions are constructed as single channel adiabatically separable eigenfunctions of readily defined distortion potentials.

The basic features of the present model are given in Sec. II. Numerical tests of the treatment for model potential energy surfaces for the I + HI and Cl + HBr reactions are given in Sec. III. The results are discussed in Sec. IV.

II. DIABATIC FORMALISM

We consider a rearrangement collision which involves a transition from a vibrational state n of the reactant molecule BC to a vibrational state m of the product molecule AB,



The Schrödinger equation can be conveniently written in terms of the two alternative sets of Jacobian mass-weighted coordinates $\{\tau_\alpha, R_\alpha\}$, $\{\tau_\beta, R_\beta\}$ appropriate for describing the reactants' and the products' configurations:

$$H = H_\alpha = -\frac{1}{2} \frac{\partial^2}{\partial R_\alpha^2} + h_\alpha(\tau_\alpha, R_\alpha); \quad h_\alpha(\tau_\alpha, R_\alpha) = -\frac{1}{2} \frac{\partial^2}{\partial \tau_\alpha^2} + V_\alpha(\tau_\alpha, R_\alpha) \quad (2.2)$$

$$H = H_\beta = -\frac{1}{2} \frac{\partial^2}{\partial R_\beta^2} + h_\beta(\tau_\beta, R_\beta); \quad h_\beta(\tau_\beta, R_\beta) = -\frac{1}{2} \frac{\partial^2}{\partial \tau_\beta^2} + V_\beta(\tau_\beta, R_\beta) .$$

where $\tau_i = m_i^{1/2} r_i'$, r_i' being the internal coordinate of the diatomic molecule ($i = \alpha$ for reactants, β for products); m_i is the reduced mass of the molecule i . Similarly $R_i = M_i^{1/2} R_i'$, R_i' being the separation between the atom and the center of mass of the diatomic molecule i ; M_i is the reduced mass of the relevant atom-diatom pair. $h_i(\tau_i, R_i)$ is a vibrational Hamiltonian for fixed R_i .

In the asymptotic region the dependence of the vibrational Hamiltonian $h_i(r_i, R_i)$ on R_i vanishes. The two h_i 's reduce to the vibrational Hamiltonian for a single diatomic molecule:

$$h_{BC}(r_a) = -\frac{1}{2} \frac{\partial^2}{\partial r_a^2} + V_a(r_a), \quad h_{AB}(r_\beta) = -\frac{1}{2} \frac{\partial^2}{\partial r_\beta^2} + V_\beta(r_\beta) \quad (2.3)$$

In the case of transfer of a light particle lying between two heavy ones (i.e., $m_B \ll m_A, m_C$) the polar coordinates (ρ, θ) ,

$$\rho = (R_a^2 + r_a^2)^{1/2} = (R_\beta^2 + r_\beta^2)^{1/2} \quad (2.4)$$

$$\theta = \tan^{-1}(r_a/R_a) = \theta_m - \tan^{-1}(r_\beta/R_\beta) \quad (2.5)$$

are, as shown elsewhere,^{19-21,24} particularly well-suited for simplifying the approximate treatment of the dynamics, due to the near-separability of the motion along the fast (θ) and slow (ρ) coordinates. The angle θ_m between the skewed axes in Fig. 1 equals $\tan^{-1}[m_\beta/(m_a M_a)^{1/2}]$. The Hamiltonian in these polar coordinates is written as

$$H = -\frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2\rho} \frac{\partial}{\partial \rho} - \frac{1}{2\rho^2} \frac{\partial^2}{\partial \theta^2} + V(\theta, \rho) \quad (2.6)$$

It is also convenient to define an arc length, measured from the R_a axis in Fig. 1, and to denote the maximum arc length by s_m :

$$s = \rho\theta; \quad s_m = \rho\theta_m \quad (2.7)$$

Asymptotically the system can be in the arrangement channel α or β . For large values of ρ one can relate the asymptotic form of Eq. (2.6) to that of Eq. (2.2) by employing the approximate relations between the polar and the Cartesian coordinates in the region relevant to the motion of the system, namely in the regions $s \ll s_m$ and $s_m - s \ll s_m$. We have there

$$R_\alpha \approx \rho, \quad r_\alpha \approx s; \quad R_\beta \approx \rho, \quad r_\beta \approx s_m - s. \quad (2.8)$$

In order to obtain the DWBA reaction amplitude for the rearrangement reaction we divide the potential energy function

$$V(s, \rho) \equiv V_\alpha(s, \rho) \equiv V_\beta(s, \rho), \quad (2.9)$$

into two parts

$$V(s, \rho) = V_\alpha^I(s, \rho) + V_\alpha^{II}(s, \rho) \quad (2.10)$$

$$V_\beta(s, \rho) = V_\beta^I(s, \rho) + V_\beta^{II}(s, \rho).$$

The distortion potential $V_i^I(s, \rho)$ includes all the distortion of the potential between the atoms in the diatomic molecule due to the proximity of the third particle but none of the interactions responsible for the rearrangement. The interaction potential $V_i^{II}(s, \rho)$ on the other hand represents solely the reactive part of the interaction which causes the rearrangement ($i = \alpha, \beta$).

We take the nonreactive wavefunctions for both arrangements to be the solutions of the Schrödinger equations with the distortion potential V_α^I only.

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2\rho} \frac{\partial}{\partial \rho} - \frac{1}{2\rho^2} \frac{\partial^2}{\partial \theta^2} + V_\alpha^I(s, \rho) \right] \psi_n^\alpha = E \psi_n^\alpha \quad (2.11)$$

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2\rho} \frac{\partial}{\partial \rho} - \frac{1}{2\rho^2} \frac{\partial^2}{\partial \theta^2} + V_\beta^I(s, \rho) \right] \psi_m^\beta = E \psi_m^\beta.$$

In the absence of the reactive interactions the motion along ρ and along s is nearly adiabatically separable within each of the valleys (reactants', products') of the potential energy surface. Thus, a good approximation to these nonreactive solutions of Eq. (2.11) can be obtained using the adiabatic approximation.²⁴

$$\psi_n^a(s, \rho) \cong \varphi_n^a(\rho) \chi_n^a(s, \rho) \quad (2.12)$$

$$\psi_m^b(s, \rho) \cong \varphi_m^b(\rho) \chi_m^b(s, \rho) .$$

where the χ 's are the eigenfunctions of the nonreactive Hamiltonian (Eq. (2.11)) for a fixed ρ and depend parametrically on ρ . They satisfy

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial s^2} + V_a^I(s, \rho) \right] \chi_n^a(s, \rho) = \epsilon_n^a(\rho) \chi_n^a(s, \rho) \quad (2.13)$$

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial s^2} + V_b^I(s, \rho) \right] \chi_m^b(s, \rho) = \epsilon_m^b(\rho) \chi_m^b(s, \rho) .$$

where we have used $ds = \rho d\theta$ in the derivative. The distorted single channel vibrational wavefunctions $\chi(s, \rho)$ are functions of s which depend parametrically on ρ . It can be readily shown that the ρ -dependent coefficients φ_n^k in Eq. (2.12) satisfy approximately the Born-Oppenheimer-like Eq. (2.14).

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2\rho} \frac{\partial}{\partial \rho} - \{E - \epsilon_n^a(\rho)\} \right] \varphi_n^a(\rho) = 0 \quad (2.14)$$

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2\rho} \frac{\partial}{\partial \rho} - \{E - \epsilon_m^b(\rho)\} \right] \varphi_m^b(\rho) = 0 .$$

The DWBA transition amplitude for the reaction is then given by

$$T_n^a \rightarrow m^b = \langle \psi_m^b | V_a^{II} | \psi_n^a \rangle , \quad (2.15)$$

where $\psi_n^a(\psi_m^b)$ is the wavefunction for the reactants (products) when the potential is the nonreactive part $V_a^I(V_b^I)$. A perturbative treatment that includes the reactive part of the potential V^{II} to the first order can be expected to give accurate results at energies below the classical threshold, where the reaction can be viewed as a perturbation to the nonreactive scattering.

Using the single channel adiabatic approximation (Eq. (2.13)) the T-matrix expression (Eq. (2.15)) for going from state n of channel α to state m of channel β can be rewritten as

$$T_{nm}^{\alpha\beta} = \int_0^\infty d\rho \varphi_m^\beta(\rho) \varphi_n^\alpha(\rho) \int_0^{s_m} ds \chi_m^\beta(s, \rho) V_\alpha^{II}(s, \rho) \chi_n^\alpha(s, \rho) \quad (2.16)$$

For every value of the radial coordinate ρ between the asymptotic region and the saddle point region, the cut along the s coordinate on the potential energy surface of a light atom transfer reaction represents a double minimum potential. We confine our attention to such ρ 's for which the cut is a double minimum potential. The boundary between "reactants" and "products" at any finite ρ is defined as the top of the barrier $s = s^b(\rho)$ in Fig. 2. We now define V_α^I in such a way as to be identical to V_α in the reactants' valley and to be a constant, namely the value of V_α at $s^b(\rho)$ in the products' valley. Similarly, V_β^I is defined at each ρ to be V_β in the products' valley and to be $V_\beta(s^b, \rho)$ in the reactants' valley. That is,

$$V_\alpha^I(s, \rho) = \begin{cases} V_\alpha(s, \rho) & s \leq s^b(\rho) \\ V_\alpha(s^b, \rho) & s > s^b(\rho) \end{cases} \quad (2.17)$$

Similarly for $V_\beta^I(s, \rho)$ we have

$$V_\beta^I(s, \rho) = \begin{cases} V_\beta(s, \rho) & s \geq s^b(\rho) \\ V_\beta(s^b, \rho) & s < s^b(\rho) \end{cases} \quad (2.18)$$

The reactive part of the potential $V_i^{II}(\rho, s)$ is then given by

$$V_i^{II} = V_i - V_i^I \quad (i = \alpha, \beta) \quad (2.19)$$

V_α^{II} vanishes for $s \leq s^b(\rho)$, for all ρ , and V_β^{II} vanishes for $s \geq s^b(\rho)$ for all ρ . Equation (2.16) then reduces to

$$T_{nm}^{\alpha\beta} = \int_0^\infty d\rho \varphi_m^\beta(\rho) \varphi_n^\alpha(\rho) \int_{s^b(\rho)}^{s_m} ds \chi_m^\beta(s, \rho) V_\alpha^{II}(s, \rho) \chi_n^\alpha(s, \rho) \quad (2.20)$$

III. APPLICATION TO I + HI AND Cl + HBr SYSTEMS

The major part of the contribution to the integral above comes from a narrow range of values of ρ near the classical turning point. We shall therefore approximate the solution of Eq. (2.14) by the solution of the equivalent equation in which the potential $(E - \epsilon_j^i)$, where $i = \alpha, \beta$ and $j = n, m$, is linearized around the classical turning-point (ρ_n^0 and ρ_m^0 for the reactants' and products' channels, respectively):

$$\begin{aligned} (E - \epsilon_n^\alpha) &= (\rho - \rho_n^0) F_n \\ (E - \epsilon_m^\beta) &= (\rho - \rho_m^0) F_m \end{aligned} \quad (3.1)$$

The F_j 's are the derivatives of $E - \epsilon_j^i$ with respect to ρ at the turning point ρ_i^0 . That is,¹⁹

$$\begin{aligned} \Psi_n^\alpha &\cong (2/B_n)^{1/2} Ai[-B_n(\rho - \rho_n^0)] \\ \Psi_m^\beta &\cong (2/B_m)^{1/2} Ai[-B_m(\rho - \rho_m^0)] \end{aligned} \quad (3.2)$$

where $B_j = (2F_j)^{2/3}$ and Ai is the Airy function.

The reaction probability is given by

$$P_{nm}^{\alpha\beta} = [2\pi T_{nm}^{\alpha\beta}]^2 \quad (3.3)$$

$$\begin{aligned} T_{nm}^{\alpha\beta} &= \frac{8\pi^2}{(B_n B_m)^{1/2}} \int_{-\infty}^{\infty} d\rho Ai[-B_m(\rho - \rho_m^0)] Ai[-B_n(\rho - \rho_n^0)] \\ &\times \int_{s^0}^{s_m} \frac{ds}{\rho} \chi_m^\beta(s, \rho) [V_\alpha(s, \rho) - V_\alpha'(s, \rho)] \chi_n^\alpha(s, \rho) \end{aligned} \quad (3.4)$$

The integral over s in Eq. (3.4),

$$V_{nm}^{\alpha\beta}(\rho) = \int_{s^0}^{s_m} \chi_m^\beta(s, \rho) [V_\alpha(s, \rho) - V_\alpha'(s, \rho)] \chi_n^\alpha(s, \rho) ds / \rho \quad (3.5)$$

was evaluated numerically. The eigenfunctions χ_n^a and χ_m^b of Eq. (2.13) were also evaluated numerically using a finite element method.²⁵ Since V_{nm}^{ab} is approximately an exponential function of ρ in the region around the turning points, a region making the principal contribution to the integral, it can be written as

$$V_{nm}^{ab} \cong V_{nm}^0 e^{-c(\rho - \rho_0^0)} , \quad (3.6)$$

where V_{nm}^0 is the value of $V_{nm}^{ab}(\rho)$ at the "average" turning point ρ_0^0 halfway between the turning points ρ_0^a and ρ_0^b . The slopes F_m and F_n for the present system are almost identical

$$F_m \cong F_n = F ; \quad B_m \cong B_n = B \quad (3.7)$$

Eq. (3.4) can then be written as

$$T_{nm}^{ab} = \frac{2V_{nm}^0}{B} \int_{-\infty}^{\infty} Ai[B(\rho - \rho_0^a)] e^{-c(\rho - \rho_0^0)} Ai[B(\rho - \rho_0^b)] d\rho , \quad (3.8)$$

which can readily be evaluated analytically¹⁹ to yield

$$T_{nm}^{ab} = \frac{V_{nm}^0}{(2\pi c F)^{1/2}} \exp\left[\frac{c^3}{24F}\right] \exp\left[-\frac{\Delta^2}{2cF}\right] . \quad (3.9)$$

Here, Δ is the value of $V_n^a(\rho) - V_m^b(\rho)$ at ρ_0^0 . More details on the (3.8) integral evaluation are given in Ref. 19, Sec. V. In the case of symmetric H-atom exchange between the same vibrational states the same formula applies with $\Delta = 0$ and, then Eq. (3.7) is exact. In the case when states n and m are far from being degenerate, Eq. (3.4) can also be readily evaluated analytically using a slightly different procedure.²⁶

The forward and the reverse transition probabilities $P_{n \rightarrow m}^{a \rightarrow b}$ and $P_{m \rightarrow n}^{b \rightarrow a}$ obtained from Eq. (3.8) are slightly different due to the lack of symmetry in the approximate Eq. (3.3). The mean of the forward and reverse proba-

bilities $P_{nm}^{a\beta}$ and $P_{mn}^{\beta a}$ was found to give a more accurate approximation to the transition probability than either $P_{nm}^{a\beta}$ or $P_{mn}^{\beta a}$ alone and is used below in the comparison of the results. Due to the closeness of the $P_{nm}^{a\beta}$ and $P_{mn}^{\beta a}$ results the particular form of the mean used (geometric or arithmetic) did not influence the result significantly.

Equation (3.8) was used to calculate the probabilities for H-atom transfer in two different collinear systems: $I + HI \rightarrow IH + I$ and $Cl + HBr \rightarrow ClH + Br$ for which accurate numerical solutions of the two-state problem are available.²³

The transition probabilities obtained by using Eq. (3.8) are presented in Figs. 3 and 4 as a function of the total energy for the IHI and $ClHBr$ systems, respectively. The results of an accurate numerical coupled channel solution of the $ClHBr$ problem²² are also given for comparison in Fig. 4. The results for the IHI system in Fig. 5 are compared with the results of an accurate numerical solution of the two state problem.¹⁹ The latter have been shown^{19,27} to be in excellent agreement with the coupled channel results on a slightly different potential energy surface for the reaction for which accurate coupled channel calculations have been performed.²⁷ The numerical results obtained for Figs. 3 and 4 using (3.6) were indistinguishable, in the Figures, from those obtained numerically using (2.16).

IV. DISCUSSION

The results presented in the preceding section demonstrate that the present simplified DWBA treatment leads to very accurate results for the reactive transition probabilities below the classical threshold. As discussed in Ref. 20 such accuracy in the threshold region is sufficient to

determine the reaction rates at low and normal temperatures for the reactions tested as well as to explain curvature of the Arrhenius plots for H-transfer reaction at low temperatures.^{15,16,28}

- The present treatment is conceptually simpler than the one we devised in Refs. 19-21 since it follows a very straightforward formulation of the DWBA distorted wavefunctions and interaction potentials. It is also computationally simpler since it does not involve evaluation of eigenfunctions of double minimum potentials. Although the eigenfunctions of the one-dimensional anharmonic potentials are evaluated in the present work numerically, approximate analytical procedures for their evaluation can also be devised.

The validity of the present method is restricted to light atom transfer reactions with moderate to high potential energy barriers to the reaction. The present formalism hinges on the possibility of defining separate vibrational states for the reactants and the products, and can not be implemented if the barrier is not appreciably larger than the zero-point vibrational energy of the reactants. The systems to which the present formalism does apply are the ones for which the tunneling contribution to the reaction rate is significant and for which the DWBA transition probabilities around the reaction threshold determine the thermal reaction rates.

The formalism presented here is not restricted to transfer between nearly degenerate vibrational states, since no such assumption is used in the derivation. Comparisons with accurate numerical results are, however, presented only for nearly degenerate and degenerate systems due to the paucity or absence of accurate results for other systems.

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FIGURE CAPTIONS

Fig. 1.

Plot indicating the various variables used on the text. The 'skewing angle' θ_m is also given.

Fig. 2.

Profile of the potential energy surface for a fixed ρ is depicted by the curve ABCD. The nonreactive surfaces $V_a^I(s, \rho)$ and $V_b^I(s, \rho)$ are given by the curves ABCG and FCDE, respectively.

Fig. 3.

Log P_{00}^R versus total energy for the $I + HI \rightarrow IH + I$ system. The circles denote the results given by Eq. (3.3) and the solid line represents the results of the numerical solution of the two-state problem.

Fig. 4.

Log P_{02}^R versus total energy for the $Cl + HBr \rightarrow ClH + Br$ system. The circles denote the results given by Eq. (3.3) and the solid line represents the results of an accurate coupled channel numerical solution of the problem.

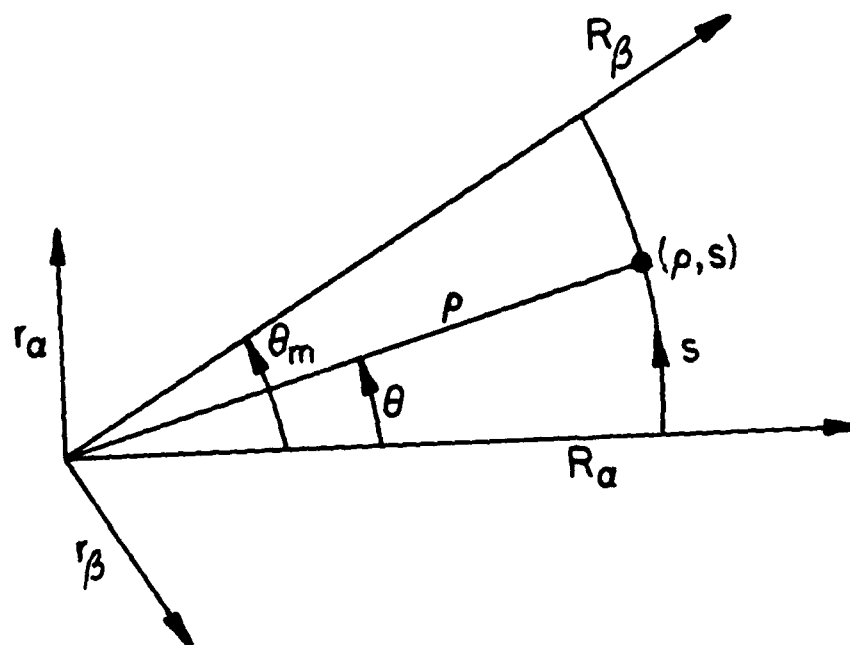


Figure 1

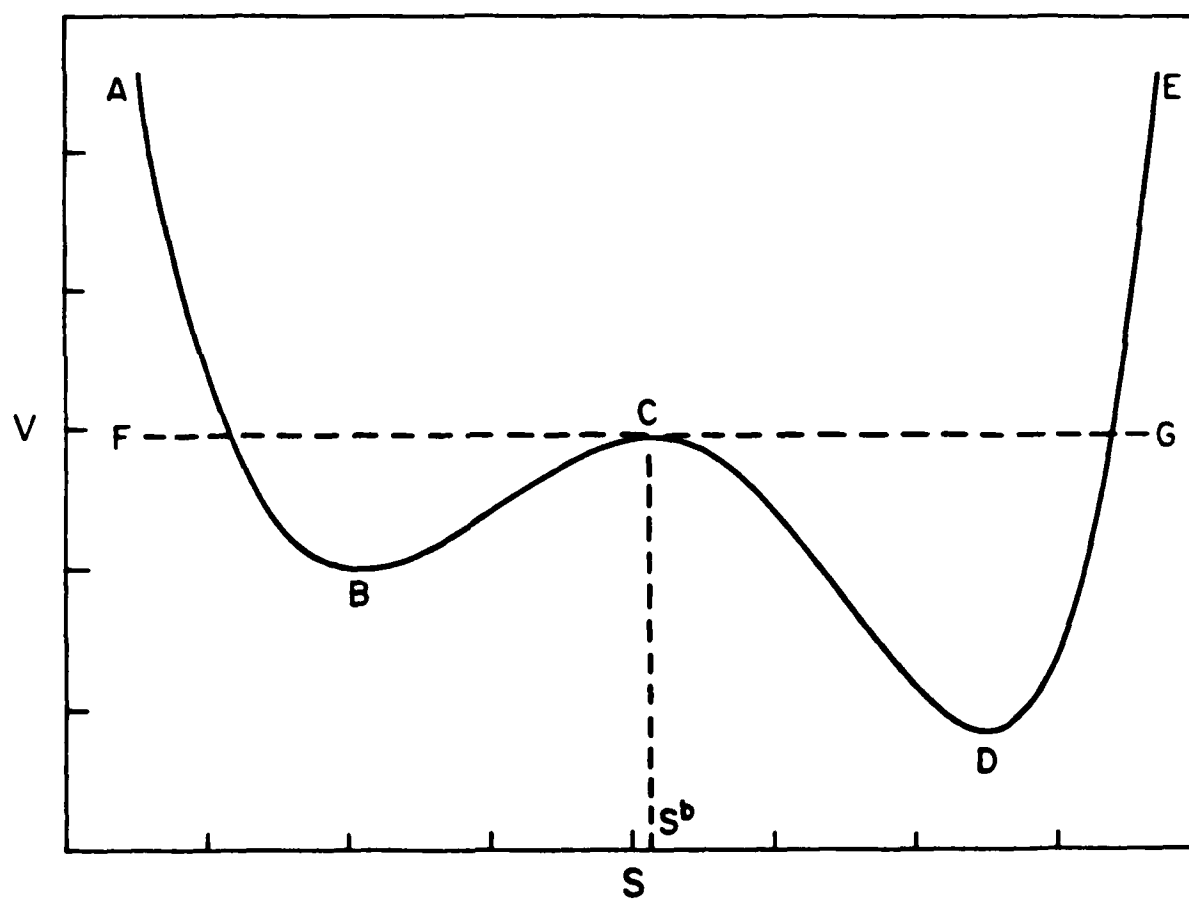


Figure 2

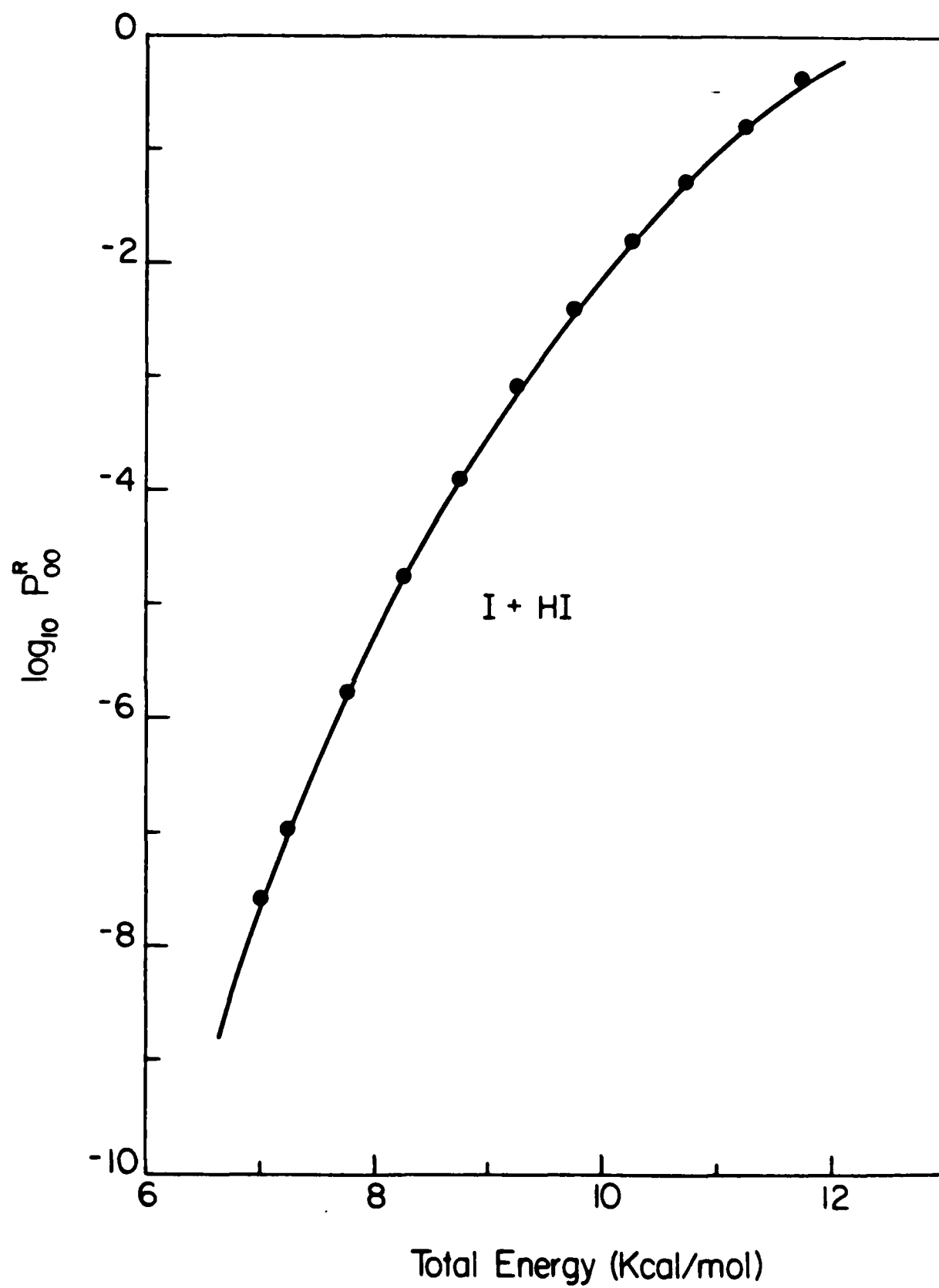


Figure 3

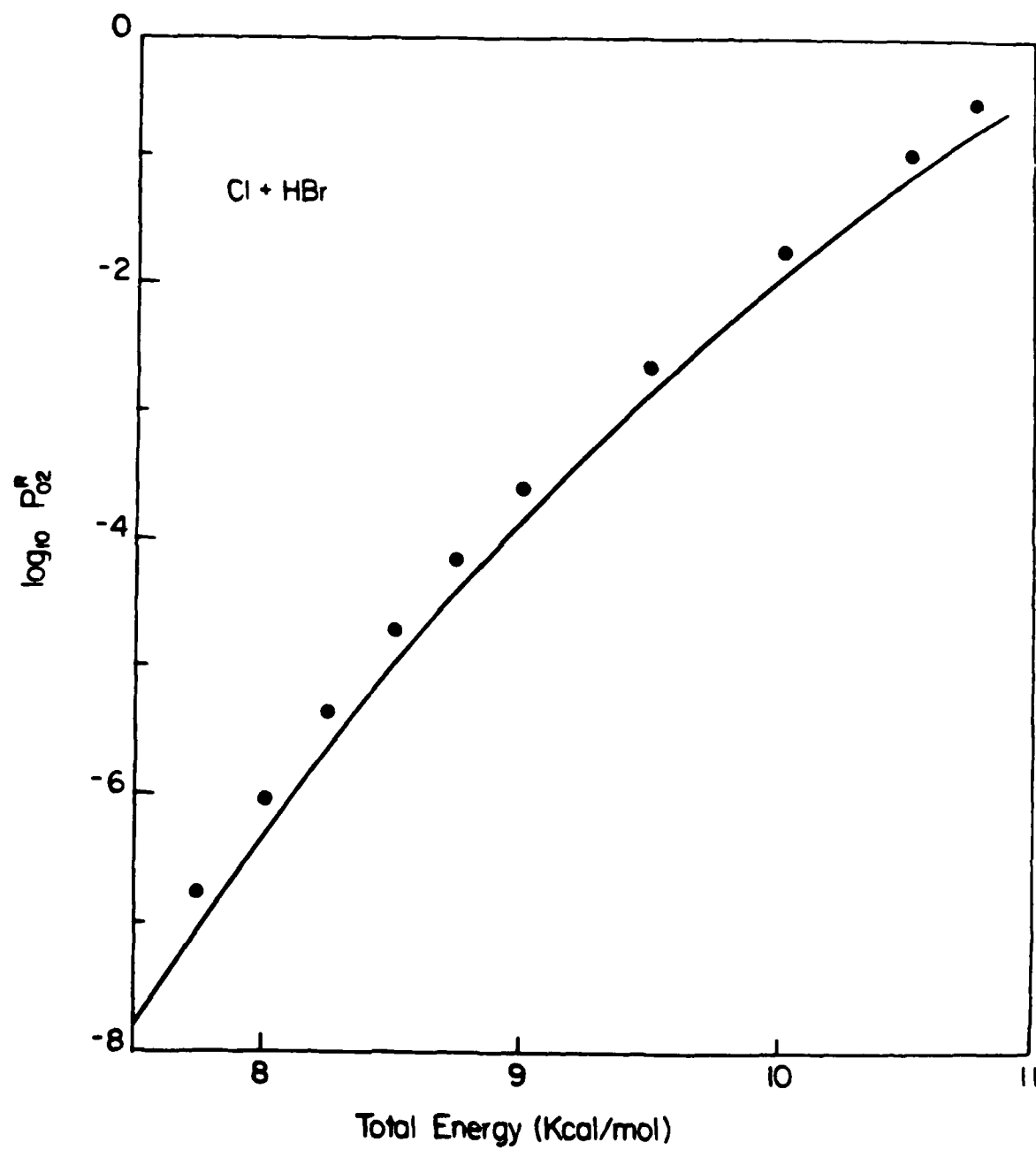


Figure 4

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